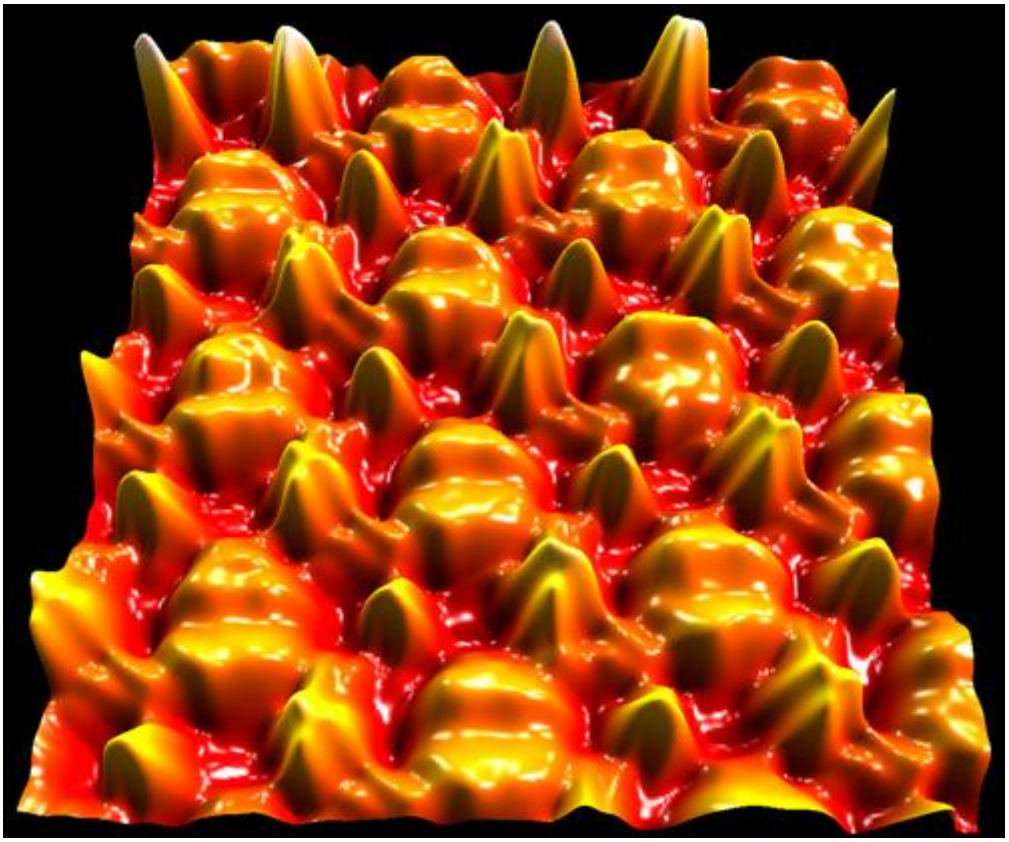
ChemComm

This article is part of the

Molecule-based Surface Chemistry web themed issue

Guest Editors include Steven De Feyter, Federico Rosei & Dmitrii Perepichka

Please visit the website to access the other articles in this issue:-
http://www.rsc.org/chemcomm/surfacechemistry



ChemComm

Dynamic Article Links

Cite this: *Chem. Commun.*, 2011, **47**, 10070–10072

www.rsc.org/chemcomm

COMMUNICATION

Single-layer graphene oxide sheet: a novel substrate for dip-pen nanolithography†‡

Hai Li,§[a] Xiehong Cao,§[a] Bing Li,[a] Xiaozhu Zhou,[a] Gang Lu,[a] Cipto Liusman,[a] Qiyuan He,[a] Freddy Boey,[ab] Subbu S. Venkatraman[a] and Hua Zhang*[ab]

Received 5th May 2011, Accepted 27th July 2011
DOI: 10.1039/c1cc12648b

Graphene oxide (GO) sheet is used as a novel substrate for dip-pen nanolithography (DPN). After GO is transferred onto SiO_2 using the Langmuir–Blodgett technique, $CoCl_2$ is patterned on both GO and exposed SiO_2 substrates simultaneously by DPN, which is used for growth of different structured carbon nanotubes.

Graphene, a one-atom-thick two-dimensional carbon sheet, has attracted increasing interest since its discovery in 2004.[1] As an insulating and disordered analogue of graphene, graphene oxide (GO) has some advantages, such as the rich functional groups, easy reduction to graphene (also called reduced GO, *i.e.* rGO), dissolution in water and other solvents, and large-amount production by using chemical methods.[2] Recently, GO and rGO have been extensively studied due to their broad applications in synthesis of nanocomposites,[3] chemical and biological sensors,[4] solar cells,[5] electric and optical devices,[6] cell cultures,[7] *etc.*

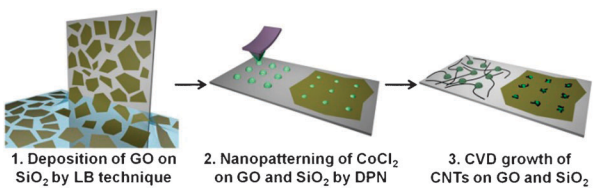
Dip-pen nanolithography (DPN),[8] a direct-write scanning probe microscopy (SPM)-based lithography, has been successfully used for controlled patterning of various materials on different substrates, such as Au, Ag, Si, SiO_2, glass, quartz, polymers, *etc.* Previous studies demonstrated that one of the key factors to affect the ink transportation of DPN is the surface property of substrates. Although it has been reported that the surface property of single-layer GO or rGO sheets plays an important role in synthesis of GO or rGO-based nanocomposites,[3a–e,k] until now there has been no report about how to directly deposit nanostructures on GO by DPN, and no study on how GO affects the ink transportation of DPN. Moreover, there is no report on patterning the same "ink" on two different surfaces simultaneously by DPN.

In this communication, by using DPN, we have patterned $CoCl_2$ simultaneously on SiO_2 and single-layer GO sheets, which are pre-adsorbed on SiO_2. The difference of ink transportation on SiO_2 and GO is investigated. Subsequently, after chemical vapor deposition (CVD), carbon nanotubes (CNTs) with different structures grown on different patterned surfaces are observed (Scheme 1). To the best of our knowledge, this is the first time to use GO as a novel substrate for the DPN study.

Scheme 1 shows the experimental procedure (see Notes for the detailed description of experiments).¶ After the single-layer GO sheets were transferred onto a cleaned SiO_2 substrate by using the Langmuir–Blodgett (LB) technique,[2c,9] $CoCl_2$ was patterned on GO and exposed SiO_2 areas simultaneously by using DPN. Then the patterned sample was used for growth of CNTs by CVD.

In order to investigate the ink transfer on GO and SiO_2, $CoCl_2$ dots were patterned on GO and SiO_2 simultaneously by DPN at different dwell times. Fig. 1A and B show AFM images of patterned $CoCl_2$ dots on GO and SiO_2, respectively, at dwell times ranging from 0.1 to 2 s. The volume of patterned $CoCl_2$ dots (V) can be calculated as follows. We assume that the $CoCl_2$ dots on GO and SiO_2 are spherical segments according to the AFM images (Fig. 1A–B) and section analysis profiles (Fig. 1D–E). The height of the $CoCl_2$ dot (h) and the size of the $CoCl_2$ dot ($2r$) can be measured from AFM images. Thus the volume of $CoCl_2$ dots (V) can be calculated by the equation for spherical segment, $v = \frac{\pi h}{6}(3r^2 + h^2)$.

As shown in Fig. 1C, V increased from $\sim 1.44 \times 10^6$ to $\sim 1.69 \times 10^7$ nm^3 on GO, and $\sim 1.43 \times 10^7$ to $\sim 4.08 \times 10^7$ nm^3 nm on SiO_2. Importantly, for the first time, we observed that the volume of patterned $CoCl_2$ dots shows a linear dependence on the square root of dwell time ($t^{1/2}$) on GO and SiO_2. Moreover, at the same dwell time, the deposited volume of $CoCl_2$ dots on GO is smaller than that on SiO_2. It can be



Scheme 1 Schematic illustration of the experimental procedure. (1) Single-layer GO sheets are transferred onto SiO_2 by using the LB technique. (2) $CoCl_2$ is simultaneously patterned on GO and SiO_2 by DPN. (3) CNTs grow on patterned catalyst dots on GO and SiO_2 after CVD.

[a] *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore. E-mail: hzhang@ntu.edu.sg, hzhang166@yahoo.com; Fax: +65-6790-9081; Tel: +65-6790-5175*
[b] *Centre for Biomimetic Sensor Science, Nanyang Technological University, 50 Nanyang Drive, Singapore 639798, Singapore*
† This article is part of the *ChemComm* 'Molecule-based surface chemistry' web themed issue.
‡ Electronic supplementary information (ESI) available: HRTEM images of MWCNT grown on rGO. See DOI: 10.1039/c1cc12648b
§ These authors contributed equally to this work.

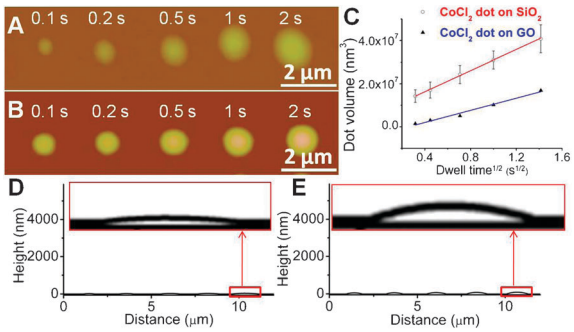


Fig. 1 AFM images of patterned $CoCl_2$ dots on (A) GO and (B) SiO_2 at dwell times of 0.1, 0.2, 0.5, 1, and 2 s. (C) Plots of the volume of patterned $CoCl_2$ dots *vs.* $t^{1/2}$ on GO and SiO_2. (D, E) Section analysis profiles of patterned $CoCl_2$ dots on (A) GO and (B) SiO_2 based on the AFM images, with *X* and *Y* axes at the same scale. Insets in (D) and (E) show the magnified images of the red boxes. It can be seen that the shape of $CoCl_2$ dots is like a spherical segment.

explained by the different surface hydrophilicity of GO and SiO_2, which affect the ink transportation of DPN. As reported previously, more hydrophilic surface leads to the faster ink transportation of DPN.[8m] As known, the water contact angle on GO is ~41°,[3h,10] which is higher than that on a fresh cleaned SiO_2 (less than 10°).[10a,11] Therefore, we believe that more hydrophilic SiO_2 leads to the faster transportation of $CoCl_2$.

As a proof of concept, the sample with DPN-patterned $CoCl_2$ dots on GO and SiO_2 was subjected to CVD for growth of CNTs. During the CVD process, $CoCl_2$ dots were reduced to Co nanoparticles (NPs), which were used as catalyst for growth of CNTs,[8o] and GO was thermally reduced to rGO.[12] Fig. 2A shows an SEM image of Co NP patterns on rGO and SiO_2, where short fiber-like structures were observed on rGO (Fig. 2B), while long CNTs were observed on SiO_2 (Fig. 2C) after CVD. High resolution transmission electron microscopy (HRTEM) image shows those fiber-like structures on rGO are multi-walled CNTs (MWCNTs) with a diameter of ~15 nm (see ESI‡). AFM image shows that the diameter of the long CNTs grown on SiO_2 is 1.7–1.9 nm (Fig. 2D), indicating the formation of single-walled CNTs (SWCNTs), which is consistent with previous reports.[8o,p] The remarkably different structure of CNTs grown on rGO and SiO_2 indicated that the different substrates, namely rGO and SiO_2, greatly influenced the growth of CNTs by CVD.

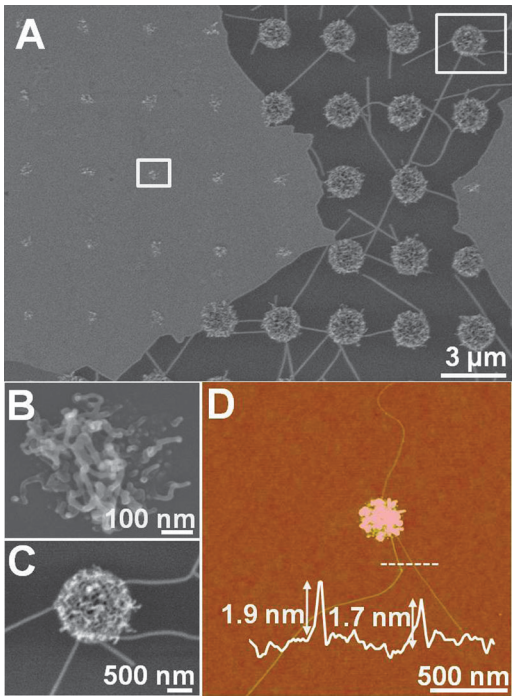


Fig. 2 (A) SEM image of Co NP catalyst dots on rGO and SiO_2 after the CVD process for growth of CNTs. Before CVD, the $CoCl_2$ dots were simultaneously patterned on GO and SiO_2 by DPN at a dwell time of 0.1 s. (B–C) Magnified SEM images of the small and large rectangular areas designated in (A). (D) AFM image of a DPN-generated $CoCl_2$ NP dot on SiO_2 after CVD. Inset: section analysis of the dashed line in (D).

In summary, $CoCl_2$ has been successfully patterned on single-layer GO sheets and SiO_2 substrate simultaneously by DPN. For the first time, we observe that the patterned volume of $CoCl_2$ dots shows a linear $t^{1/2}$ dependence on both GO and SiO_2, indicating that the ink transportation of DPN is not only in the lateral direction, but also in the vertical direction. The surface hydrophilicity of GO and SiO_2 plays an important role in the ink transportation, resulting in a slower deposition rate of $CoCl_2$ on GO. After CVD, different structured CNTs grow on SiO_2 and rGO, proving the influence of substrates on the growth of CNTs. To the best of our knowledge, this is first time to demonstrate GO as a novel substrate for DPN, which is then used as a substrate for growth of MWCNTs. This novel graphene/CNT composite might have potential applications in sensing, solar cells, electrode materials, *etc.*

This work was supported by AcRF Tier 2 (ARC 10/10, No. MOE2010-T2-1-060) from MOE, CRP (NRF-CRP2-2007-01) from NRF, A*STAR SERC Grant (No. 092 101 0064) from A*STAR, and New Initiative Fund FY 2010 (M58120031) from NTU in Singapore.

Notes and references

¶ *Substrate preparation*. After the SiO_2 substrates were sonicated in a mixture of acetone and water (v : v = 1 : 1) for 15 min, they were immersed in a piranha solution (mixture of 98% H_2SO_4 and 30% H_2O_2 at v : v = 7 : 3) at 120 °C for 1 h (**Caution**: strongly corrosive), which then were thoroughly washed with Milli-Q water (18.2 MΩ cm) and dried with nitrogen gas. The cleaned substrates were used for adsorption of graphene oxide (GO) sheets immediately. *Synthesis of graphene oxide (GO) and its assembly on SiO_2 substrate by the Langmuir–Blodgett (LB) technique*. After a small amount of expandable graphite (Bay Carbon, Bay City, MI) was sealed in a glass vial and purged with high purity nitrogen for 2 h, it was heated in a microwave oven (Sanyo, model EM-G3597v, 800 W) for less than 20 s. Graphene oxide (GO) was synthesized from the microwave-expanded graphite by the modified Hummers method.[3c,13] The synthesized GO was redispersed in a mixed solution of water and methanol (1 : 5) and then assembled onto a freshly cleaned SiO_2 substrate using the Langmuir–Blodgett (LB) technique.[9] Briefly, GO solution (8–12 mL) was dropped at a rate of 100 μL min^{-1} onto a water surface in the LB trough (KSV5000, KSV Instruments Ltd., Finland). After compression of the GO film on H_2O with a surface pressure of 15 mN m^{-1}, a freshly cleaned SiO_2 substrate was vertically dipped into the solution and then slowly pulled out (1 mm min^{-1}) to form a single-layer GO film on the SiO_2 substrate. *DPN experiments and AFM imaging*. In a typical experiment, after a Si_3N_4 tip (DNP, Veeco Inc., CA; force constant: 0.58 N m^{-1}) was immersed in the mixture of 0.1 M $CoCl_2$, 0.5 M tricine and 0.3% agarose solution (v : v : v = 1 : 1 : 3) for 2 min and subsequently slightly drying with N_2, $CoCl_2$ was successfully coated on the Si_3N_4 tip. In order to facilitate the patterning of $CoCl_2$

by DPN, the $CoCl_2$-coated tip was incubated at room temperature in a sealed box at a relative humidity (RH) of 90% for 40 min,[8a] and then used to pattern $CoCl_2$ at 90% RH. DPN experiments were carried out by using the NSCRIPTOR DPN system (Nanoink Inc., IL). A commercial AFM instrument (Dimension 3100 with Nanoscope IIIa controller, Veeco Instruments Inc., CA) equipped with a scanner ($90 \times 90\ \mu m^2$) was used to image the samples in tapping mode in air. Si cantilevers with the normal resonance frequency of 300 kHz and spring constant of 40 N m^{-1} (Tap300Al-G, Budget Sensors®, Innovative Solutions Bulgaria Ltd., Bulgaria) were used. All images were captured with a scan rate at 1–2 Hz and with 512×512 pixel resolution. *Growth of CNTs by CVD*. The growth of CNTs was performed by CVD, as described in our previous studies.[8o,14] The DPN-patterned substrates were placed in the middle of a quartz tube furnace with a diameter of 1 inch. The temperature was gradually increased to 900 °C in the mixed Ar/H_2 gas flow (200 sccm/100 sccm). After purging for 30 min to eliminate trace amounts of O_2/CO_2 and stabilize the catalyst, the Ar/H_2 flow rate was reduced to 100 sccm/50 sccm. The ethanol vapor (carbon source) was then introduced by bubbling the Ar/H_2 (100 sccm/50 sccm) gas mixture into a glass vacuum-trap ethanol bottle. After CVD for 20–40 min, CNTs grew on the catalyst patterns. The furnace was subsequently cooled down to room temperature under Ar flow. *SEM characterization*. SEM was performed using a JEOL JSM-7600 field-emission scanning electron microanalyzer at accelerating voltage of 1 and 5 kV, respectively.

1 (*a*) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666–669; (*b*) A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183–191; (*c*) X. Huang, Z. Y. Yin, S. X. Wu, X. Y. Qi, Q. Y. He, Q. C. Zhang, Q. Y. Yan, F. Boey and H. Zhang, *Small*, 2011, **7**, 1876–1902; (*d*) X. Huang, X. Y. Qi, F. Boey and H. Zhang, *Chem. Soc. Rev.*, DOI: 10.1039/C1CS15078B.

2 (*a*) D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228–240; (*b*) K. P. Loh, Q. L. Bao, G. Eda and M. Chhowalla, *Nat. Chem.*, 2011, **2**, 1015–1024; (*c*) F. Kim, L. J. Cote and J. X. Huang, *Adv. Mater.*, 2010, **22**, 1954–1958.

3 (*a*) Y. Li, X. Li, C. Dong, J. Y. Qi and X. J. Han, *Carbon*, 2010, **48**, 3427–3433; (*b*) X. Huang, X. Z. Zhou, S. X. Wu, Y. Y. Wei, X. Y. Qi, J. Zhang, F. Boey and H. Zhang, *Small*, 2010, **6**, 513–516; (*c*) X. Zhou, X. Huang, X. Qi, S. Wu, C. Xue, F. Y. C. Boey, Q. Yan, P. Chen and H. Zhang, *J. Phys. Chem. C*, 2009, **113**, 10842–10846; (*d*) X. Y. Qi, K. Y. Pu, H. Li, X. Z. Zhou, S. X. Wu, Q. L. Fan, B. Liu, F. Boey, W. Huang and H. Zhang, *Angew. Chem., Int. Ed.*, 2010, **49**, 9426–9429; (*e*) J. F. Shen, Y. Z. Hu, M. Shi, N. Li, H. W. Ma and M. X. Ye, *J. Phys. Chem. C*, 2010, **114**, 1498–1503; (*f*) N. L. Yang, J. Zhai, M. X. Wan, D. Wang and L. Jiang, *Synth. Met.*, 2010, **160**, 1617–1622; (*g*) S. Chen, J. W. Zhu, X. D. Wu, Q. F. Han and X. Wang, *ACS Nano*, 2010, **4**, 2822–2830; (*h*) L. J. Cote, R. Cruz-Silva and J. X. Huang, *J. Am. Chem. Soc.*, 2009, **131**, 11027–11032; (*i*) I. V. Lightcap, T. H. Kosel and P. V. Kamat, *Nano Lett.*, 2010, **10**, 577–583; (*j*) X. Y. Qi, K. Y. Pu, X. Z. Zhou, H. Li, B. Liu, F. Boey, W. Huang and H. Zhang, *Small*, 2010, **6**, 663–669; (*k*) X. Huang, S. Z. Li, Y. Z. Huang, S. X. Wu, X. Z. Zhou, S. Z. Li, C. L. Gan, F. Boey, C. A. Mirkin and H. Zhang, *Nat. Commun.*, 2011, **2**, 292; (*l*) S. X. Wu, Z. Y. Yin, Q. Y. He, G. Lu, X. Z. Zhou and H. Zhang, *J. Mater. Chem.*, 2011, **21**, 3467–3470; (*m*) S. X. Wu, Z. Y. Yin, Q. Y. He, X. Huang, X. Z. Zhou and H. Zhang, *J. Phys. Chem. C*, 2011, **114**, 11816–11821; (*n*) S. X. Wu, Z. Y. Yin, Q. Y. He, G. Lu, Q. Y. Yan and H. Zhang, *J. Phys. Chem. C*, DOI: 10.1021/jp201667p.

4 (*a*) Q. Y. He, H. G. Sudibya, Z. Y. Yin, S. X. Wu, H. Li, F. Boey, W. Huang, P. Chen and H. Zhang, *ACS Nano*, 2010, **4**, 3201–3208; (*b*) J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Q. Wei and P. E. Sheehan, *Nano Lett.*, 2008, **8**, 3137–3140; (*c*) J. D. Fowler, M. J. Allen, V. C. Tung, Y. Yang, R. B. Kaner and B. H. Weiller, *ACS Nano*, 2009, **3**, 301–306; (*d*) X. Z. Zhou, Y. Y. Wei, Q. Y. He, F. Boey, Q. C. Zhang and H. Zhang, *Chem. Commun.*, 2010, **46**, 6974–6976; (*e*) Z. J. Wang, X. Z. Zhou, J. Zhang, F. Boey and H. Zhang, *J. Phys. Chem. C*, 2009, **113**, 14071–14075; (*f*) Z. J. Wang, J. Zhang, P. Chen, X. Z. Zhou, Y. L. Yang, S. X. Wu, L. Niu, Y. Han, L. H. Wang, P. Chen, F. Boey, Q. C. Zhang, B. Liedberg and H. Zhang, *Biosens. Bioelectron.*, 2011, **26**, 3881–3886; (*g*) Q. Y. He, S. X. Wu, S. Gao, X. H. Cao, Z. Y. Yin, H. Li, P. Chen and H. Zhang, *ACS Nano*, 2011, **5**, 5038–5044; (*h*) X. H. Cao, Q. Y. He, W. H. Shi, B. Li, Z. Y. Zeng, Y. M. Shi, Q. Y. Yan and H. Zhang, *Small*, 2011, **7**, 1199–1202; (*i*) G. Lu, H. Li, C. Liusman, Z. Y. Yin, S. X. Wu and H. Zhang, *Chem. Sci.*, 2011, DOI: 10.1039/C1SC00254F; (*j*) H. G. Sudibya, Q. Y. He, H. Zhang and P. Chen, *ACS Nano*, 2011, **5**, 1990–1994.

5 (*a*) Z. Y. Yin, S. X. Wu, X. Z. Zhou, X. Huang, Q. C. Zhang, F. Boey and H. Zhang, *Small*, 2010, **6**, 307–312; (*b*) Z. Y. Yin, S. Y. Sun, T. Salim, S. X. Wu, X. Huang, Q. Y. He, Y. M. Lam and H. Zhang, *ACS Nano*, 2010, **4**, 5263–5268; (*c*) J. L. Song, Z. Y. Yin, Z. J. Yang, P. Amaladass, S. X. Wu, J. Ye, Y. Zhao, W. Q. Deng, H. Zhang and X. W. Liu, *Chem.–Eur. J.*, DOI: 10.1002/chem.201101263.

6 (*a*) G. Eda and M. Chhowalla, *Adv. Mater.*, 2010, **22**, 2392–2415; (*b*) B. Li, X. H. Cao, H. G. Ong, J. W. Cheah, X. Z. Zhou, Z. Y. Yin, H. Li, J. L. Wang, F. Boey, W. Huang and H. Zhang, *Adv. Mater.*, 2010, **22**, 3058–3061; (*c*) J. Q. Liu, Z. Q. Lin, T. J. Liu, Z. Y. Yin, X. Z. Zhou, S. F. Chen, L. H. Xie, F. Boey, H. Zhang and W. Huang, *Small*, 2010, **6**, 1536–1542.

7 S. Agarwal, X. Z. Zhou, F. Ye, Q. Y. He, G. C. K. Chen, J. Soo, F. Boey, H. Zhang and P. Chen, *Langmuir*, 2010, **26**, 2244–2247.

8 (*a*) H. Li, Q. Y. He, X. H. Wang, G. Lu, C. Liusman, B. Li, F. Boey, S. S. Venkatraman and H. Zhang, *Small*, 2011, **7**, 226–229; (*b*) H. Zhang, K. B. Lee, Z. Li and C. A. Mirkin, *Nanotechnology*, 2003, **14**, 1113–1117; (*c*) D. S. Ginger, H. Zhang and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2004, **43**, 30–45; (*d*) K. Salaita, Y. H. Wang and C. A. Mirkin, *Nat. Nanotechnol.*, 2007, **2**, 145–155; (*e*) R. Sistiabudi and A. Ivanisevic, *Adv. Mater.*, 2008, **20**, 3678–3681; (*f*) Z. Zheng, J. W. Jang, G. Zheng and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2008, **47**, 9951–9954; (*g*) X. Z. Zhou, Y. H. Chen, B. Li, G. Lu, F. Y. C. Boey, J. Ma and H. Zhang, *Small*, 2008, **4**, 1324–1328; (*h*) A. J. Senesi, D. I. Rozkiewicz, D. N. Reinhoudt and C. A. Mirkin, *ACS Nano*, 2009, **3**, 2394–2402; (*i*) E. Bellido, R. de Miguel, D. Ruiz-Molina, A. Lostao and D. Maspoch, *Adv. Mater.*, 2010, **22**, 352–355; (*j*) R. A. Vega, C. K. F. Shen, D. Maspoch, J. G. Robach, R. A. Lamb and C. A. Mirkin, *Small*, 2007, **3**, 1482–1485; (*k*) K. H. Kim, J. D. Kim, Y. J. Kim, S. H. Kang, S. Y. Jung and H. Jung, *Small*, 2008, **4**, 1089–1094; (*l*) S. F. Li, S. Szegedi, E. Goluch and C. Liu, *Anal. Chem.*, 2008, **80**, 5899–5904; (*m*) J. R. Hampton, A. A. Dameron and P. S. Weiss, *J. Am. Chem. Soc.*, 2006, **128**, 1648–1653; (*n*) W. C. M. Wang, R. M. Stoltenberg, S. H. Liu and Z. N. Bao, *ACS Nano*, 2008, **2**, 2135–2142; (*o*) B. Li, C. F. Goh, X. Z. Zhou, G. Lu, H. Tantang, Y. H. Chen, C. Xue, F. Y. C. Boey and H. Zhang, *Adv. Mater.*, 2008, **20**, 4873–4878; (*p*) I. Kuljanishvili, D. A. Dikin, S. Rozhok, S. Mayle and V. Chandrasekhar, *Small*, 2009, **5**, 2523–2527; (*q*) J. H. Lim and C. A. Mirkin, *Adv. Mater.*, 2002, **14**, 1474–1477; (*r*) X. Z. Zhou, F. Boey and H. Zhang, *Chem. Soc. Rev.*, 2011, DOI: 10.1039/C1CS15045F; (*s*) X. Z. Zhou, F. Boey, F. W. Huo, L. Huang and H. Zhang, *Small*, 2011, DOI: 10.1002/smll.201002381.

9 (*a*) L. J. Cote, F. Kim and J. X. Huang, *J. Am. Chem. Soc.*, 2009, **131**, 1043–1049; (*b*) G. Lu, X. Z. Zhou, H. Li, Z. Y. Yin, B. Li, L. Huang, F. Boey and H. Zhang, *Langmuir*, 2010, **26**, 6164–6166.

10 (*a*) J. F. Ou, J. Q. Wang, S. Liu, B. Mu, J. F. Ren, H. G. Wang and S. R. Yang, *Langmuir*, 2010, **26**, 15830–15836; (*b*) S. A. Hasan, J. L. Rigueur, R. R. Harl, A. J. Krejci, I. Gonzalo-Juan, B. R. Rogers and J. H. Dickerson, *ACS Nano*, 2010, **4**, 7367–7372.

11 (*a*) K. Y. Suh, A. Khademhosseini, G. Eng and R. Langer, *Langmuir*, 2004, **20**, 6080–6084; (*b*) X. J. Zhang and D. G. Cahill, *Langmuir*, 2006, **22**, 9062–9066.

12 (*a*) D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R. D. Piner, S. Stankovich, I. Jung, D. A. Field, C. A. Ventrice Jr and R. S. Ruoff, *Carbon*, 2009, **47**, 145–152; (*b*) D. H. Lee, J. E. Kim, T. H. Han, J. W. Hwang, S. Jeon, S.-Y. Choi, S. H. Hong, W. J. Lee, R. S. Ruoff and S. O. Kim, *Adv. Mater.*, 2010, **22**, 1247–1252.

13 (*a*) B. Li, G. Lu, X. Zhou, X. Cao, F. Boey and H. Zhang, *Langmuir*, 2009, **25**, 10455–10458; (*b*) H. Li, J. Zhang, X. Z. Zhou, G. Lu, Z. Y. Yin, G. P. Li, T. Wu, F. Boey, S. S. Venkatraman and H. Zhang, *Langmuir*, 2010, **26**, 5603–5609; (*c*) W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

14 (*a*) X. H. Cao, B. Li, Y. Z. Huang, F. Boey, T. Yu, Z. X. Shen and H. Zhang, *ACS Appl. Mater. Interfaces*, 2009, **1**, 1873–1877; (*b*) B. Li, X. H. Cao, X. Huang, G. Lu, Y. Z. Huang, C. F. Goh, F. Y. C. Boey and H. Zhang, *Small*, 2009, **5**, 2061–2065.

